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Enhanced high-solids anaerobic digestion of waste activated sludge by the addition of scrap iron

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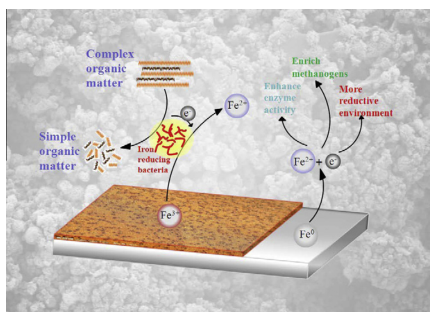
HIGHLIGHTS

- A new method to accelerate the anaerobic digestion of sludge without pretreatment.
- Iron scrap has better mass transformation efficiency than iron powder.
- *Acetobacteria* and iron-reducing bacteria can be enriched by rusty scrap.
- Adding rusty scrap made the methane production raise 29.51%.

GRAPHICAL ABSTRACT



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ABSTRACT

Anaerobic digestion of waste activated sludge usually requires pretreatment procedure to improve the bioavailability of sludge, which involves considerable energy and high expenditures. This study proposes a cost-effective method for enhanced anaerobic digestion of sludge without a pretreatment by directly adding iron into the digester. The results showed that addition of Fe^0 powder could enhance 14.46% methane yield, and Fe scrap (clean scrap) could further enhance methane yield (improving rate 21.28%) because the scrap has better mass transfer efficiency with sludge and liquid than Fe^0 powder. The scrap of Fe with rust (rusty scrap) could induce microbial Fe(III) reduction, which resulted in achieving the highest methane yield (improving rate 29.51%), and the reduction rate of volatile suspended solids (VSS) was also highest (48.27%) among Fe powder, clean scrap and rusty scrap. PCR–DGGE proved that the addition of rusty scrap could enhance diversity of *acetobacteria* and enrich iron-reducing bacteria to enhance degradation of complex substrates.

1. Introduction

Yield of waste activated sludge generated in biological wastewater treatment processes has increased continuously in the recent decade, due to increasing population in cities and towns and construction of new waste water treatment plants (WWTPs). The total dry sludge amount in European Union countries has reached more than 10 million tons per year (Duan et al., 2012). In China, over 11.2 million tons of dry sludge is generated annually and almost 80% of it has not obtained necessary stabilization (Zhang et al., 2012). To minimize the volume of waste sludge, most municipal sludge (such as more than 80% in China) before discharge is dewatered to get high-solid sludge with total solid content typically greater than 10% (w/w). However, there is still a large amount

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of biodegradable compounds contained in the dewatering sludge which gives rise to secondary pollution including leaching of liquid and odor (Lee and Han, 2013).

Anaerobic digestion of waste sludge is an efficient and sustainable technology to stabilize sludge by means of mass reduction and methane production simultaneously. Methane is an alternative energy source to limited fossil fuels which helps cut down the operation cost of treatment plants. However, the application of anaerobic digestion of sludge is often limited by low methane yield and sludge reduction rate (Duan et al., 2012). The limiting factors are generally associated with the slow hydrolysis of sludge. To improve the rate-limiting hydrolysis and digestion performance, many types of pretreatments such as chemical, mechanical and biological sludge disintegration have been developed (Lagerkvist and Morgan-Sagastume, 2012). Pretreatment may result in lysis or disintegration of sludge cells, thus releasing and solubilizing intracellular material into the water phase and transforming refractory organic materials into biodegradable species, and therefore making more materials readily available for microorganisms. However, mechanical and thermal methods require the input of considerable amount of energy (Weemaes and Verstraete, 1998). Chemical treatment, including acid/alkali hydrolysis, ozone and advanced oxidation, requires large amount of chemicals to maintain the reaction conditions (Navia et al., 2002). The operating cost of the present pretreatment is high and often not easy to be acceptable for application.

Fe^0, which is a cheap reductant, was found to be able to accelerate anaerobic hydrolysis of simple and soluble materials when it was added into the anaerobic system (Liu et al., 2012; Zhang et al., 2011a). The mechanism was that Fe^0 could decrease oxidative-reductive potential (ORP) to create a more favorable environment for anaerobic digestion. The activity of the enzymes associated with hydrolysis–acidification was observed to increase 2–34 times with the addition of Fe^0 powder (Meng et al., 2013). It was possible that the Fe^0 could accelerate the anaerobic digestion of sludge because Fe^0 might enhance the hydrolysis–acidification. Moreover, Fe^0 was reported to enhance the growth of methanogens to increase methane production (Chastain and Kral, 2010). In previous work, adding Fe^0 powder in an anaerobic digestion of diluted sludge (1% solid content) after pretreatment by alkaline was confirmed to enhance methane production (Feng et al., 2014). However, there has been no study that investigated the effects of Fe^0 on sludge digestion without a pretreatment till date. It is unknown whether addition of Fe^0, especially iron scrap, could replace the tedious pretreatment processes mentioned above to enhance anaerobic digestion of high-solid sludge. If scrap or waste scrap iron could directly accelerate the sludge digestion, it is expected to provide a practical and economical alternative to reduce the complicated and high-cost procedures prior to digestion. In this study, the performance of anaerobic digestion of high-solid sludge was investigated in comparison with adding different types of iron including Fe^0 powder, clean scrap and rusty scrap. Also, the microorganism communities functioning in the anaerobic digestion were identified and explored.

2. Methods

2.1. Substrates and inoculum

Dewatered sewage sludge from the Chunliu Wastewater Treatment Plant (Dalian, China) was used as substrates for this study. The inoculums were collected from an anaerobic digester at a Waste Sludge Treatment Plant of Dalian (China). Before the digestion, the substrates were mixed with the inoculum in a ratio of 9:1. Two batch tests were conducted, and characteristics of sludge mixture are listed in Table 1.

2.2. Preparation of iron

Three kinds of iron were used: Fe^0 powder, clean scrap and rusty scrap (see Fig. S1, Supporting Information). The Fe^0 powder (diameter of 0.2 mm, BET surface area of 0.05 m^2/g, purity > 98%) was purchased from Shenyang Chemical Reagent Plant. The iron scrap (about 8 mm × 4 mm × 0.5 mm, purity > 95%) was obtained from a machinery workshop. Before the use, the scrap was soaked in 0.1 mol/L of NaOH solution for 24 h to remove oil and then washed with dilute HCl solution and tap water to remove the rusty cover. The rusty scrap (about 8 mm × 4 mm × 0.5 mm) was the same as the clean scrap mentioned above but without rust removal. In other words, the rusty scrap had a corrosion layer covering the surface of the scrap.

2.3. Batch experiments

The mixture (200 mL) of substrates and inoculum was incubated in 250 mL serum bottles placed in an air-bath shaker (120 rpm) at 35 ± 1 °C for 22 days. After adding a certain amount of iron (in the form of the powder, clean scrap or rusty scrap), the bottles were capped with silica gel stoppers and oxygen was removed from the headspace by exchanging it with nitrogen gas for 10 min. A silica tube across the silica gel stoppers was connected to the gasbag. During the digestion, the biogas produced from each bottle was collected into gasbag for analysis.

Two batch experiments were conducted in this study. The first experiment was to investigate the effects of different dosage of Fe^0 powder and the clean scrap on anaerobic sludge digestion under seven dosage levels (0, 1, 6, 8, 10, 14 and 20 g/L). The other experiment was conducted to compare the effect of the clean and rusty scrap under a specific dosage (10 g/L). All experiments conducted triplicate at the same time.

2.4. Analytical methods

Sludge samples from the reactors were analyzed for pH, ORP, total suspended solid (SS), volatile suspended solids (VSS), total protein and total polysaccharide. Then the samples were centrifuged at 8000 rpm for 10 min and immediately filtered through a 0.45 μm pore size cellulose membrane filters for analyzing soluble chemical oxygen demand (SCOD), soluble protein, soluble polysaccharide and VFAs. SS, VSS and SCOD were determined according to Standard Methods (APHA, 1998). The ORP was immediately measured by an ORP combination class-body redox electrode (Sartorius PY-R01, Germany) after the batch experiment was finished. The pH was recorded using a pH analyzer (Sartorius PB-20, Germany). The settlement percentage of sludge was tested using 25 mL of sludge. To avoid the highly dense and no homogenous of sludge, the sludge was fully mixed before sampling and the settling time was extended from generally 30–60 min. The settlement experiment was conducted under the optimal iron dose (10 g/L). Proteins were measured with a Lowry's method using bovine serum albumin as a standard solution (Fr et al., 1995). Polysaccharides were measured with phenol–sulfuric acid method using glucose as a standard solution (Masuko et al., 2005). After the batch experiment, the reminding iron scraps was recovered by a magnet, and then it was cleaned, dried and weighed to calculate the consumption of iron. Fe^{2+} and total iron were analyzed by an adaptation of the ferrozine technique (Cooper et al., 2000). The concentration of CH_4 and CO_2 in the biogas was analyzed with a gas chromatograph (Shimadzu, GC-14C) equipped with a thermal conductivity detector and a 1.5 m stainless-steel column (Molecular Sieve, 80/100 mesh). The temperatures of injector, detector and column were kept at 100, 105 and 60 °C according to the reference (Zhao and Yu, 2008). Nitrogen was used as the carrier gas at a flow rate